Ion Exchange Kinetics.* A Nonlinear Diffusion Problem. II. Particle Diffusion Controlled Exchange of Univalent and Bivalent Ions

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The differential equation derived previously which describes the particle diffusion controlled ion exchange between spherical beads of uniform size and a well-stirred solution is solved numerically for the exchange of monovalent ions for bivalent ions, and of bivalent ions for monovalent ions. The approach is based on the Nernst-Planck equations of ionic motion. Numerical results for six different mobility ratios are presented and discussed. They were obtained by use of a digital computer. An explicit equation approximating the numerical data is given.

I. INTRODUCTION

IN a preceding paper,[1] we have used the Nernst-Planck flux equations to derive a differential equation which describes the particle-diffusion controlled exchange of ions of different mobility and arbitrary valence in spherical ion exchanger beads of uniform size. In contrast to previous theories, in which a constant interdiffusion coefficient within the bead had been assumed, our approach takes into account the electric potential gradient built up by the process which produces a variable interdiffusion coefficient. In view of other simplifying assumptions involved, which we have discussed in detail, the solutions of this equation should be considered as ideal limiting laws only. In the preceding paper, numerical solutions were given for the exchange of ions of equal valence. In this paper, we present solutions for the exchange of univalent ions for bivalent ions, and of bivalent ions for univalent ions.

II. FORMULATION OF THE PROBLEM

The dimensionless equation describing the particle-diffusion controlled exchange of two counter ion species A and B, as given by Eq. (7) in the preceding paper, is

$$\frac{\partial\gamma}{\partial\tau}-\frac{1}{1+a\gamma}\left[(1+b\gamma)\frac{\partial^2\gamma}{\partial\rho^2}+\frac{b-a}{1+a\gamma}\left(\frac{\partial\gamma}{\partial\rho}\right)^2+\frac{2(1+b\gamma)}{\rho}\frac{\partial\gamma}{\partial\rho}\right]=0, \quad (1)$$

where the dimensionless variables γ, ρ, and τ are defined by

$$\gamma\equiv z_AC_A/C; \qquad \tau\equiv D_At/r_0^2; \qquad \rho\equiv r/r_0;$$

and the dimensionless constants a and b by

$$a\equiv z_AD_A/z_BD_B-1; \qquad b\equiv z_A/z_B-1.$$

C_i is the molar concentration of the species i in the exchanger; C is defined as $z_AC_A+z_BC_B$ (total equivalent concentration); z_i is the valence of the species i; t is the time; r is the radial spherical coordinate; and r_0 is the radius of the bead.

Alternatively, Eq. (1) can be written in the form

$$\frac{\partial\gamma}{\partial\tau}-\frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left[\frac{1+b\gamma}{1+a\gamma}\rho^2\frac{\partial\gamma}{\partial\rho}\right]=0, \quad (2)$$

which is used in this paper. The quantity

$$(1+b\gamma)/(1+a\gamma)$$

is the interdiffusion coefficient in dimensionless form.

The fraction $q_A(\tau)$ of the species A still present in the sphere at the dimensionless time τ is given by Eq. (8) of the preceding paper,

$$q_A(\tau)=3\int_0^1\gamma(\rho,\tau)\rho^2d\rho. \quad (3)$$

The rate of ion exchange is given by Eq. (9) of the preceding paper,

$$-\frac{dQ_A}{dt}=-\frac{VCD_A}{r_0^2}\frac{dq_A}{d\tau}, \quad (4)$$

where Q_A is the amount of A present in the beads, and V the total volume of the beads.

We have used the same initial and boundary conditions as in the previous calculations,

$$0\leq\rho<1, \qquad \tau=0, \qquad \gamma(\rho)=1, \quad (5a)$$

$$\rho\geq1, \qquad \tau\geq0, \qquad \gamma(\rho,\tau)=0, \quad (5b)$$

corresponding to uniform presaturation of the beads with the counter ion A only, and to a solution containing, throughout the process, the counter ion B only (infinite solution volume, or continuous renewal of the solution). Other initial conditions will be treated in Sec. V.

We have evaluated Eq. (2) numerically for six different cases,

$$z_A/z_B=\tfrac{1}{2}, \qquad D_A/D_B=5, 10, 20,$$

$$z_A/z_B=2, \qquad D_A/D_B=\tfrac{1}{5}, \tfrac{1}{10}, \tfrac{1}{20}.$$

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[1] F. Helfferich and M. S. Plesset, J. Chem. Phys. **28**, 418 (1958).

The first three cases correspond to processes in which a monovalent ion initially present in the exchanger is replaced by a bivalent ion; the latter three cases correspond to the reverse processes in which a bivalent ion is replaced by a monovalent ion. It is known that the mobilities of bivalent ions in ion exchangers are considerably smaller than those of monovalent ions.[2] Therefore the calculations have been restricted to such cases. The results are given in Sec. IV.

III. CALCULATION PROCEDURE

For the numerical evaluation, Eq. (1) was approximated by the finite difference form

$$\gamma(\rho,\tau+\Delta\tau)=\gamma(\rho,\tau)+(\Delta\tau/\Delta\rho^2)\{R_+D_+[\gamma(\rho+\Delta\rho,\tau)-\gamma(\rho,\tau)]-R_-D_-[\gamma(\rho,\tau)-\gamma(\rho-\Delta\rho,\tau)]\},\quad(6)$$

where

$$R_+(\rho)\equiv[(\rho+\tfrac{1}{2}\Delta\rho)/\rho]^2;\qquad R_-(\rho)\equiv[(\rho-\tfrac{1}{2}\Delta\rho)/\rho]^2$$

and

$$D_+(\gamma)\equiv\left(\frac{1+b\gamma}{1+a\gamma}\right)_{\rho+\frac{1}{2}\Delta\rho,\tau}=\frac{2+b[\gamma(\rho+\Delta\rho,\tau)+\gamma(\rho,\tau)]}{2+a[\gamma(\rho+\Delta\rho,\tau)+\gamma(\rho,\tau)]};$$

$$D_-(\gamma)\equiv\left(\frac{1+b\gamma}{1+a\gamma}\right)_{\rho-\frac{1}{2}\Delta\rho,\tau}=\frac{2+b[\gamma(\rho,\tau)+\gamma(\rho-\Delta\rho,\tau)]}{2+a[\gamma(\rho,\tau)+\gamma(\rho-\Delta\rho,\tau)]}.$$

The initial condition is

$$\gamma(\rho,\tau=0)=1\qquad(0\leq\rho<1),\quad(7)$$

TABLE I. Fractional attainment of equilibrium $F(\tau)$ and dimensionless rate $-dq_A(\tau)/d\tau$ for six different values of the ratios z_A/z_B and D_A/D_B ($z_A/z_B=\frac{1}{2}$, $D_A/D_B=20$).

τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$
0.00006812	0.014	109.8	0.09856	0.491	2.11
0.0002703	0.028	54.4	0.1106	0.515	1.95
0.001075	0.055	26.8	0.1266	0.545	1.77
0.002200	0.078		0.1466	0.578	1.59
0.003028	0.094		0.1666	0.608	1.44
0.003992	0.109	13.1	0.1866	0.636	1.32
0.004915	0.123		0.2046	0.659	1.22
0.006391	0.139		0.2366	0.695	1.08
0.008728	0.161		0.2686	0.728	0.960
0.01223	0.190		0.3006	0.757	0.863
0.01656	0.213	6.22	0.3246	0.777	0.799
0.02056	0.243	5.43	0.3486	0.795	0.742
0.02656	0.274	4.74	0.3966	0.828	0.642
0.03256	0.300	4.21	0.4446	0.857	0.558
0.03856	0.324	3.82	0.5086	0.890	0.464
0.04656	0.353	3.42	0.5486	0.907	0.412
0.05456	0.379	3.10	0.5886	0.923	0.366
0.06256	0.403	2.85	0.6686	0.949	0.282
0.07456	0.435	2.54	0.7486	0.968	0.208
0.08656	0.464	2.31	0.8286	0.982	0.140
			0.9086	0.991	0.082

[2] G. E. Boyd and B. A. Soldano, J. Am. Chem. Soc. **75**, 6091 (1953).

TABLE II. Fractional attainment of equilibrium $F(\tau)$ and dimensionless rate $-dq_A(\tau)/d\tau$ for six different values of the ratios z_A/z_B and D_A/D_B ($z_A/z_B=\frac{1}{2}$, $D_A/D_B=10$).

τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$
0.00003467	0.012	185.2	0.07263	0.504	2.91
0.0001382	0.024	91.9	0.08063	0.527	2.71
0.0005522	0.048	45.4	0.09263	0.558	2.45
0.001287	0.074	29.1	0.09863	0.572	2.33
0.002193	0.094	22.2	0.1086	0.595	2.17
0.003443	0.121	17.2	0.1186	0.615	2.02
0.004756	0.141	14.6	0.1286	0.635	1.90
0.006318	0.162	12.3	0.1386	0.653	1.78
0.008630	0.185	10.6	0.1506	0.674	1.66
0.01063	0.212	9.37	0.1626	0.693	1.55
0.01363	0.238	8.20	0.1746	0.711	1.46
0.01663	0.261	7.33	0.1986	0.744	1.29
0.02063	0.289	6.47	0.2266	0.778	1.13
0.02563	0.319	5.70	0.2586	0.812	0.978
0.02963	0.341	5.22	0.2906	0.841	0.851
0.03663	0.375	4.58	0.3386	0.877	0.693
0.04263	0.401	4.16	0.3866	0.907	0.564
0.04863	0.425	3.82	0.4506	0.939	0.419
0.05663	0.454	3.46	0.5306	0.966	0.270
0.06463	0.480	3.16	0.6106	0.983	0.154
			0.6906	0.992	0.078

and the boundary conditions at the bead surface and at the bead center are

$$\gamma(\rho=1,\tau)=0;\qquad\gamma(\rho=0,\tau)=\gamma(\rho=0+\Delta\rho,\tau).\quad(8)$$

The stability condition for the numerical calculation[3] is given by

$$\Delta\tau=0.4\Delta\rho^2/D_{\max},\quad(9)$$

where $D_{\max}$ is the maximum possible value of the dimensionless interdiffusion coefficient,

$$D_{\max}=1\qquad\text{for}\quad a>0,\quad b<0,\quad\text{and}$$

$$D_{\max}=\frac{1+b}{1+a}\qquad\text{for}\quad a<0,\quad b>0.\quad(10)$$

By use of Eqs. (6) through (10), the function $\gamma(\rho,\tau)$ can be calculated. The procedure outlined here is somewhat more efficient than that used in our previous calculations[1] because exponential functions have been avoided.

For the numerical integration corresponding to Eq. (3), Simpson's rule was used

$$q_A(\tau)=(\Delta\rho)^3\left[4\sum_{n=1,3,5\cdots}^{1/\Delta\rho-1}n^2\gamma(\rho,\tau)+2\sum_{n=2,4,6\cdots}^{1/\Delta\rho-2}n^2\gamma(\rho,\tau)\right],\quad(11)$$

where

$$n\equiv\rho/\Delta\rho.$$

The dimensionless rate, $-dq_A/d\tau$, was approximated by

$$-dq_A/d\tau=[q_A(\tau-\Delta\tau)-q_A(\tau)]/\Delta\tau.\quad(12)$$

[3] Courant, Friedrichs, and Lewy, Math. Ann. **100**, 32 (1928).

TABLE III. Fractional attainment of equilibrium $F(\tau)$ and dimensionless rate $-dq_A(\tau)/d\tau$ for six different values of the ratios z_A/z_B and D_A/D_B ($z_A/z_B=\frac{1}{2}$, $D_A/D_B=5$).

τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$
0.00001807	0.010	301.5	0.04259	0.461	4.62
0.00007275	0.020	149.3	0.04859	0.487	4.22
0.0002876	0.041	74.3	0.05659	0.519	3.79
0.0006314	0.061	48.9	0.06459	0.548	3.44
0.001147	0.082	36.4	0.07059	0.568	3.22
0.001772	0.101	28.4	0.07659	0.587	3.02
0.002522	0.121	23.7	0.08459	0.610	2.80
0.003460	0.141	20.1	0.09259	0.632	2.60
0.004585	0.163	17.4	0.1006	0.652	2.43
0.006585	0.197	14.3	0.1086	0.670	2.28
0.008585	0.224	12.3	0.1166	0.688	2.14
0.01059	0.247	10.9	0.1286	0.712	1.95
0.01259	0.267	9.88	0.1406	0.735	1.79
0.01459	0.286	9.06	0.1526	0.756	1.65
0.01659	0.304	8.40	0.1766	0.792	1.42
0.01859	0.320	7.84	0.2006	0.824	1.22
0.02259	0.349	6.96	0.2286	0.855	1.03
0.02659	0.376	6.29	0.2590	0.884	0.860
0.03059	0.399	5.75	0.2974	0.913	0.679
0.03459	0.422	5.31	0.3454	0.941	0.494
0.03859	0.442	4.94	0.4014	0.964	0.325
			0.5374	0.990	0.099

TABLE V. Fractional attainment of equilibrium $F(\tau)$ and dimensionless rate $-dq_A(\tau)/d\tau$ for six different values of the ratios z_A/z_B and D_A/D_B ($z_A/z_B=2$, $D_A/D_B=\frac{1}{10}$).

τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$
0.000004688	0.009	1167.0	0.01519	0.503	12.7
0.00001836	0.019	585.4	0.01669	0.521	11.8
0.00007305	0.038	289.4	0.01969	0.554	10.3
0.0002918	0.079	140.8	0.02299	0.586	8.98
0.0004318	0.108	104.2	0.02509	0.604	8.29
0.0006918	0.127	87.8	0.02779	0.625	7.55
0.001092	0.157	68.8	0.03079	0.646	6.84
0.001592	0.188	55.7	0.03379	0.666	6.24
0.002292	0.223	45.1	0.03679	0.684	5.73
0.003092	0.256	37.7	0.04279	0.715	4.87
0.003692	0.277	33.8	0.04879	0.743	4.20
0.004292	0.296	30.8	0.05679	0.773	3.50
0.004892	0.314	28.3	0.06479	0.799	2.96
0.005492	0.330	26.3	0.07079	0.816	2.64
0.006292	0.350	24.0	0.08279	0.844	2.12
0.007092	0.369	22.1	0.09779	0.872	1.65
0.008692	0.402	19.3	0.1178	0.900	1.22
0.01069	0.437	16.6	0.1378	0.922	0.921
0.01269	0.468	14.6	0.1738	0.948	0.580
0.01369	0.483	13.8	0.2238	0.970	0.322
			0.3400	0.990	0.099

As in the previous calculations, a very fine subdivision of space and time was required initially. The initial spacing of ρ used was $\Delta\rho=1/1280$. The spacing of τ was selected in accordance with the stability condition (9). As the calculation proceeded, $\Delta\rho$ was increased stepwise to 1/640, 1/320, 1/160, 1/80, 1/40 (at about $q_A=0.9$), and 1/20 (at about $q_A=0.4$). $\Delta\tau$ was increased correspondingly. The estimated maximum error in q_A is ± 0.005, the error in $dq_A/d\tau$ is about $\pm 2\%$. To arrive at this estimate, the solution to the linear case ($D_A=D_B$) was calculated by the numerical procedure and compared with the exact analytical solution; the maximum deviation was 0.0013 in q_A and less than 1% in $dq_A/d\tau$. In all calculations, a mass check was made by approximating $q_A(\tau)$ in another way

$$q_A(\tau) = q_A(\tau-\Delta\tau) - 3D\left[\gamma(1-\tfrac{1}{2}\Delta\rho, \tau)\right]\frac{\gamma(1-\Delta\rho, \tau)-\gamma(1, \tau)}{\Delta\rho}. \quad (13)$$

TABLE IV. Fractional attainment of equilibrium $F(\tau)$ and dimensionless rate $-dq_A(\tau)/d\tau$ for six different values of the ratios z_A/z_B and D_A/D_B ($z_A/z_B=2$, $D_A/D_B=\frac{1}{5}$).

τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$
0.00002295	0.019	480.0	0.02317	0.558	8.99
0.00009170	0.039	237.0	0.02717	0.592	7.85
0.0003667	0.080	115.3	0.03037	0.616	7.12
0.0005267	0.103	94.4	0.03317	0.635	6.57
0.0009667	0.137	68.5	0.03817	0.665	5.74
0.001367	0.162	56.6	0.04117	0.682	5.32
0.001967	0.192	46.1	0.04517	0.702	4.83
0.002367	0.210	41.4	0.04917	0.721	4.41
0.003167	0.240	34.9	0.05717	0.753	3.37
0.003567	0.253	32.5	0.06317	0.774	3.29
0.004767	0.289	27.3	0.06917	0.792	2.94
0.005967	0.319	23.7	0.07817	0.817	2.50
0.006767	0.337	21.9	0.08417	0.831	2.26
0.007567	0.354	20.3	0.09317	0.850	1.95
0.009167	0.385	17.9	0.1112	0.880	1.48
0.01117	0.418	15.6	0.1352	0.910	1.06
0.01357	0.453	13.6	0.1502	0.925	0.866
0.01477	0.469	12.8	0.2002	0.957	0.469
0.01637	0.488	11.8	0.2587	0.977	0.244
0.01957	0.524	10.3	0.3562	0.991	0.087

TABLE VI. Fractional attainment of equilibrium $F(\tau)$ and dimensionless rate $-dq_A(\tau)/d\tau$ for six different values of the ratios z_A/z_B and D_A/D_B ($z_Az_B=2$, $D_AD_B=\frac{1}{20}$).

τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$	τ	$F(\tau)$	$-\frac{dq_A(\tau)}{d\tau}$
0.000003919	0.009	1364.0	0.01474	0.516	13.0
0.00001564	0.019	677.0	0.01662	0.539	11.8
0.00006173	0.038	335.6	0.01873	0.560	10.5
0.0002400	0.077	165.3	0.02089	0.582	9.72
0.0003900	0.102	123.1	0.02329	0.604	8.84
0.0006400	0.129	96.6	0.02569	0.624	8.05
0.0009400	0.155	78.7	0.02809	0.643	7.37
0.001340	0.183	64.6	0.03289	0.675	6.27
0.001740	0.207	55.5	0.03889	0.709	5.24
0.002040	0.223	50.5	0.04589	0.743	4.35
0.002540	0.247	44.3	0.05589	0.781	3.43
0.003040	0.267	39.6	0.06189	0.801	3.01
0.003540	0.286	36.0	0.07689	0.840	2.25
0.004540	0.319	30.7	0.08589	0.858	1.31
0.005740	0.354	26.2	0.1099	0.896	1.30
0.007140	0.387	22.6	0.1249	0.914	1.04
0.008640	0.419	19.7	0.1609	0.943	0.645
0.009390	0.433	18.5	0.2209	0.970	0.315
0.01044	0.452	17.1	0.3229	0.990	0.105
0.01249	0.484	14.9			

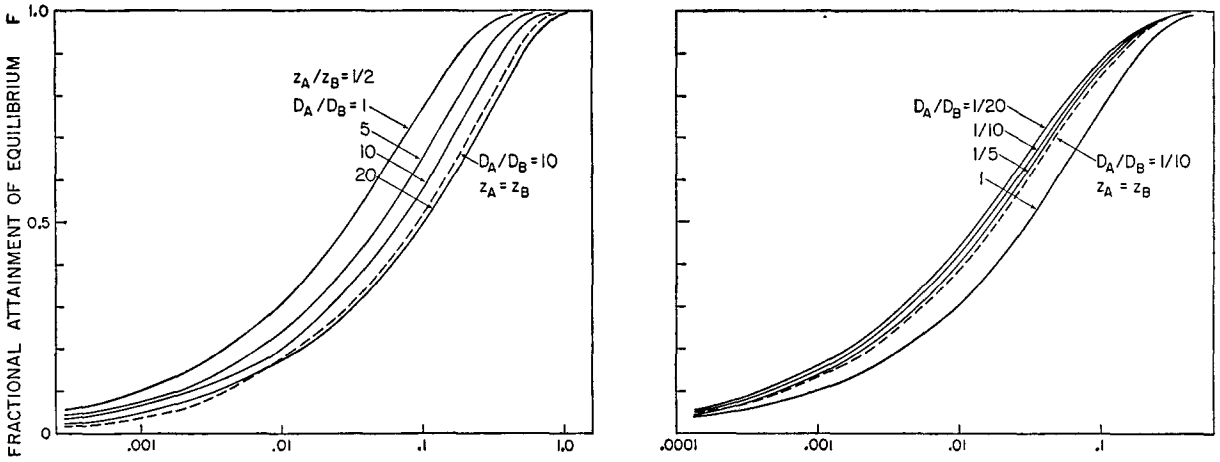

FIG. 1. Fractional attainment of equilibrium as a function of the dimensionless time coordinate $\tau=D_A t/r_0^2$ (on logarithmic scale) for $z_A/z_B=\frac{1}{2}$(left) and $z_A/z_B=2$(right). The different curves correspond to different values of the ratio D_A/D_B. For comparison, the curves for the exchange of ions of equal valence and $D_A/D_B=10$ and $1/10$, respectively, are given as broken lines.

This slightly less accurate way of calculating $q_A(\tau)$ (it is equivalent to the use of the trapezoidal rule instead of Simpson's rule) gave values within ± 0.018 of the values calculated according to Eq. (11).

The calculations were carried out on the Datatron digital computer (manufactured by Electrodata, Inc., Pasadena, California) in the computing center at the California Institute of Technology. Floating point numbers were used. The total machine time required was about 35 hours.

IV. RESULTS AND DISCUSSION

As in the preceding paper, we have kept the presentation of the results in dimensionless form. The actual values of the concentration C_A and C_B, the fractional attainment of equilibrium, and the rate at a given time t can be obtained from the tables and graphs by substituting numerical values for D_A, r_0, C, and V.

The Tables I to VI give the fractional attainment of equilibrium, $F(\tau)=1-q_A(\tau)$, and the dimensionless rate, $-dq_A/d\tau$, as functions of the dimensionless time τ for the various cases. Figure 1 shows a graph of F *versus* τ, and also shows the solutions for two of the cases calculated previously, in which both counter ion species have the same valence. If $D_A=D_B$, the diffusion equation is linear regardless of ionic valence so that the familiar analytical solution applies; this solution is also shown in Fig. 1. The radial concentration profiles of the ion A present in the bead initially are plotted in Fig. 2. A comparison of the exchange of Na^+ for Ca^{2+} and its reverse process, the exchange of Ca^{2+} for Na^+, is given in Fig. 3 where, for both processes, the fractional attainment of equilibrium is plotted as a function of the time coordinate $D_{Na}t/r_0^2$. For these curves, a mobility ratio $D_{Na}/D_{Ca}=10$ was assumed which corresponds roughly to the situation in commercial ion exchange resins.[2]

When the rates calculated for the exchange of ions of different valence and of equal valence (solid lines and dotted lines, respectively, in Fig. 1) for the mobility ratio $D_A/D_B=10$ and $D_A/D_B=1/10$ are compared, it is seen that the exchange of ions of different valence occurs at a higher rate, no matter whether the bivalent ion is initially in the exchanger or in the solution. This effect is to be expected. Figure 1 of reference 1 shows that, for given individual diffusion constants D_A and D_B and for given equivalent fraction of A or B, the interdiffusion coefficient is greater when the slower ion has the higher valence. The explanation of this effect is straightforward. The electric field built up by the diffusion process enhances the diffusion of the slower ion and retards the diffusion of the faster ion. The force with which the electric field acts on an ion is proportional to its valence. Thus, in an exchange of ions of different valence either the flux of the slower ion is more strongly increased or the flux of the faster ion less strongly reduced by the electric field than in the exchange of ions of equal valence. If the ion of higher valence were the faster one, the opposite reasoning would hold; however, this situation is of little practical significance.

The shape of the concentration profiles (Fig. 2) depends strongly on the mobility ratio D_A/D_B of the two counter ion species involved, as has been discussed in detail in the preceding paper. The profiles seem to be little affected by ionic valence. For a given ratio D_A/D_B and a given value of the fractional attainment of equilibrium, the profiles calculated for the exchange of ions of different valence coincide roughly with the profiles calculated for the exchange of ions of equal valence (compare Fig. 4 of reference 1).

The comparison of an exchange with its reverse process in Fig. 3 shows that the rate is faster when the faster ion (Na^+) is present in the exchanger initially. Similar to the situation encountered with ions of equal valence, a difference by the factor 10 in the ionic mo-

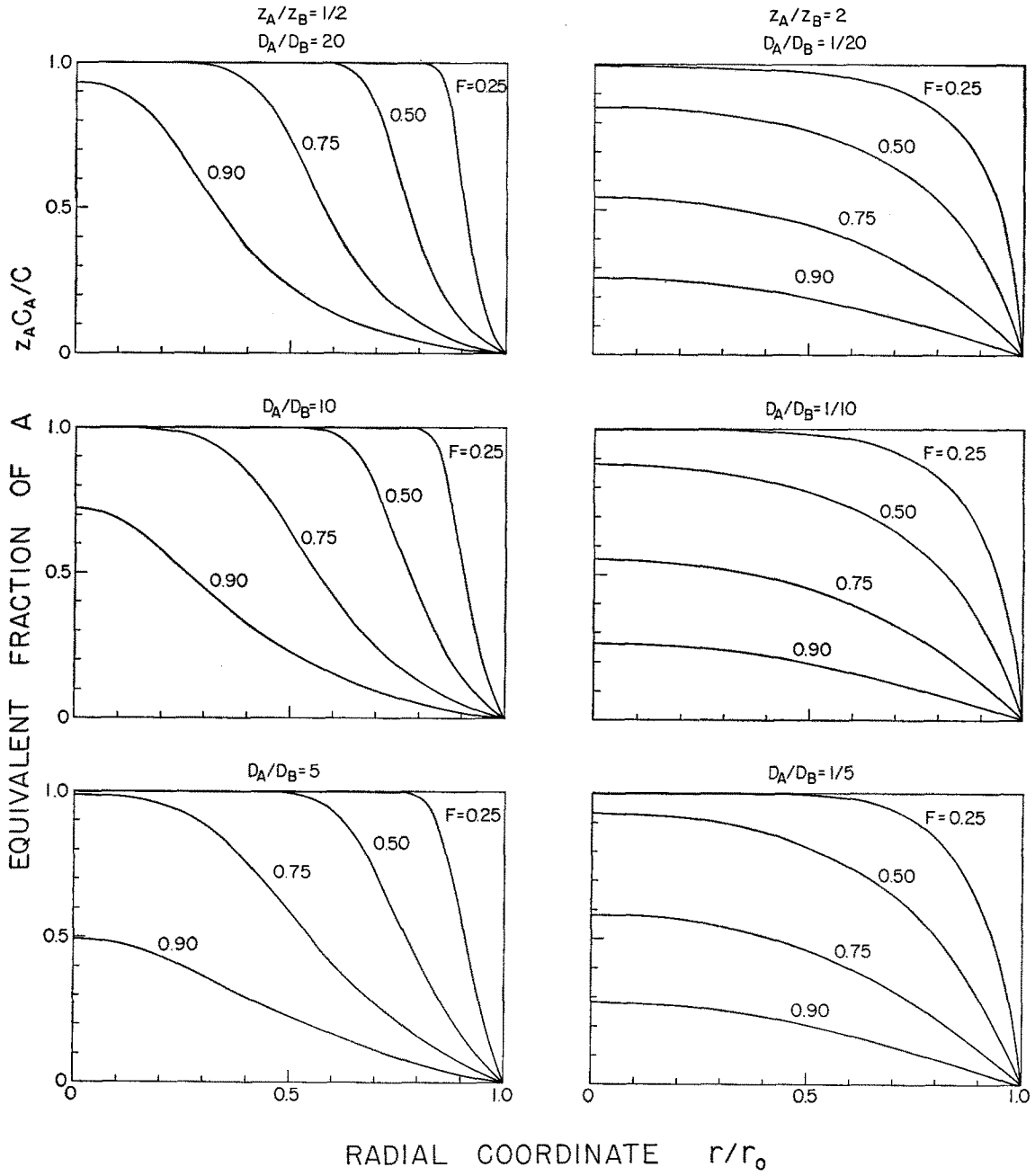

FIG. 2. Radial concentration profiles of the species A in the bead for 25, 50, 75, and 90% exchange ($F=0.25$, 0.50, 0.75, and 0.90) for different values of the ratios z_A/z_B and D_A/D_B.

bilities results in half-times of exchange that differ by about the factor 2, and to times required for 90% exchange that differ by about the factor 3.

For practical purposes, an explicit expression for $F(\tau)$ which approximates the numerical results will be useful. As in the case of the exchange of ions of equal valence, the relation

$$F(\tau)=\{1-\exp[\pi^2(f_1(\alpha)\tau+f_2(\alpha)\tau^2+f_3(\alpha)\tau^3)]\}^{\frac{1}{2}} \quad (14)$$

can be used. Here, α is D_A/D_B. For $z_A/z_B=\frac{1}{2}$, the coefficients $f_1(\alpha)$, $f_2(\alpha)$, and $f_3(\alpha)$ are given by

$$1/f_1(\alpha)=-0.64-0.36\alpha^{0.668}$$
$$1/f_2(\alpha)=-0.96+2.0\alpha^{0.4635}$$
$$1/f_3(\alpha)=-0.27-0.09\alpha^{1.140}. \quad (15)$$

Equations (14) and (15) fit all the numerical results within an error of ± 0.012 in $F(\tau)$ and may be expected to hold equally well for intermediate values of the ratio D_A/D_B within the range $1\leq D_A/D_B\leq 20$. For $z_A/z_B=2$,

a satisfactory fit was obtained only by using two different sets of coefficients,

$$\left.\begin{aligned} 1/f_1(\alpha) &= -0.350-0.650\alpha^{0.860} \\ 1/f_2(\alpha) &= 0.030+1.012\alpha^{2.06} \\ 1/f_3(\alpha) &= -0.00265-0.354\alpha^{2.671} \end{aligned}\right\}, \text{ for } 0\leq\tau\leq 0.04 \quad (16)$$

and

$$\left.\begin{aligned} 1/f_1(\alpha) &= -0.438-0.562\alpha^{0.7767} \\ 1/f_2(\alpha) &= 0.127+0.915\alpha^{1.057} \\ 1/f_3(\alpha) &= 0.0080-0.365\alpha^{0.4532} \end{aligned}\right\}, \quad \text{for } \tau\geq 0.04. \quad (17)$$

The maximum deviation from the numerical results is 0.006 in $F(\tau)$. Within the range $1/20\leq D_A/D_B\leq 1/5$, Eqs. (14), (16), and (17) should hold equally well for intermediate values of the ratio D_A/D_B, whereas the interpolation in the range $1/5\leq D_A/D_B\leq 1$ is somewhat less reliable.

V. EXTENSION TO OTHER INITIAL CONDITIONS

As in the case of an exchange of ions of equal valence, an extension to other initial conditions is possible in principle. If the initial distribution as a uniform partial presaturation of the beads with the ion B present in the solution

$$\begin{aligned} \tau=0, \quad & 0\leq\rho<1 \quad & \gamma(\rho)=\gamma_0 \\ & \rho\geq 1 \quad & \gamma(\rho,\tau)=0, \end{aligned} \quad (18)$$

where γ_0 may have any constant value in the range $0\leq\gamma_0\leq 1$, new constants $a'=a\gamma_0$ and $b'=b\gamma_0$ and the new variable $\gamma'=\gamma/\gamma_0$ can be defined. Then the quantity γ' satisfies the same differential equation and the same initial and boundary values as in the problem described in the previous sections. The solution of the differential equation is in terms of a', b', and γ'. However, the tables and the approximation (14) cannot be evaluated directly, because the dependence of the coefficients f_1, f_2, and f_3 on b (or b', respectively) is not accurately known. A linear interpolation between $b'=0$ (the solution for this case is given in reference 1‡) and $b'=-\frac{1}{2}$ or $b'=1$ is expected to give fair results. The calculation procedure described in this paper can be applied without changes to obtain more accurate results, simply by substituting a' and b' for a and b.

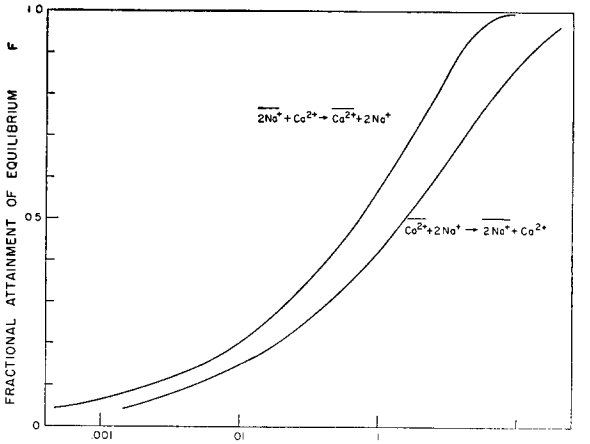

FIG. 3. Fractional attainment of equilibrium for the exchange process $Na^+(resin)+Ca^{2+}(solution\rightarrow Ca^{2+}(resin)+Na^+(solution)$ and the reverse process $Ca^{2+}(resin)+Na^+(solution\rightarrow Na^+(resin)+Ca^{2+}(solution)$, assuming a ratio $D_{Na}/D_{Ca}=10$, as a function of the time coordinate $D_{Na}t/r_0^2$. In the first case (upper curve) the exchange is faster.

VI. ACKNOWLEDGMENTS

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‡ It should be noted that the equation for the coefficient $f_2(\alpha)$ in Eq. (21a) in reference 1 should read, $1/f_2(\alpha)=0.260+0.782\alpha$.